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Document Number 8

Entry 8 of 45

File: USPT

Feb 27, 1996

DOCUMENT-IDENTIFIER: US 5494526 A

TITLE: Method for cleaning semiconductor wafers using liquified gases

DEPR:

For the removal of organic contaminants, liquefied carbon dioxide or any of the freon family of gases can be used. A variety of other organic gases can also be used to dissolve and remove organic contaminants. The system of the present invention can also be used to remove metallic contaminants by using liquefied hydrochloric acid, hydrofluoric acid or sulphur dioxide. Ionic dissociation of several acidic liquefied gases (e.g. HCL, HB.sub.r, HF, SO.sub.3) is significant at cryogenic temperatures. In some cases such as for HCL the ionic concentrations may be too high. Thus, it may be necessary to dilute or buffer the liquefied gases with other inert liquefied gases or alkaline liquefied gases such as ammonia. The use of these highly caustic compounds can be buffered by using liquefied ammonia or other alkaline agents to balance the acidity of the cleaning agent. This buffering will prevent the cleaning agent from attacking the internal surfaces of cleaning chamber 12 and can be also used to carefully control the damage to the semiconductor substrate 16 caused during the cleaning process.

CCOR:

134/1

CCXR:

134/21

CCXR:

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CCXR:

134/902

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Document Number 16

Entry 16 of 45

File: USPT

Jul 9, 1991

DOCUMENT-IDENTIFIER: US 5030319 A

TITLE: Method of oxide etching with condensed plasma reaction product

DEPR:

First, a SF.sub.4 gas is produced by discharging SF.sub.6 gas; and this SF.sub.4 gas reacts with H.sub.2 O to produce SO.sub.2 gas. The SO.sub.2 gas is combined with O atoms which are formed from H.sub.2 O by a discharge; and SO.sub.3 is produced as a result. This SO.sub.3 gas is easily condensed due to its low vapor pressure; so it may be easily deposited on the sample surface. A part of the SO.sub.3 deposited on the surface may react with H.sub.2 O to produce liquid H.sub.2 SO.sub.4. On the other hand, HF gas is produced as a result of a reaction between the H.sub.2 O and F atoms produced by said discharge, or by the abovementioned reaction between SF.sub.4 +H.sub.2 O.

DEPR:

In this way, this invention forms a condensed layer on the surface of a sample, and then etches an oxide film of the sample. It is preferable that a reactor pressure is higher and a sample temperature lower. With a high reactor pressure, gases such as H.sub.2 O, SO.sub.3 and HF more frequently hit the surface of the sample, thereby easily forming H.sub.2 SO.sub.4 that is containing HF, on the surface of the sample. Furthermore, if the reactor pressure is too low and gases including fluorine or oxygen elements are used, the fluorine or oxygen atoms produced by the electric discharge are transported to the sample to etch or oxidize Si of the sample. This hinders a selective etching of SiO.sub.2. If the reactor pressure is high, the fluorine and oxygen atoms frequently collide against other gases before reaching the sample and react with those gases to become stable fluoride and oxide gases. Accordingly, Si of the sample is not etched and oxidized. When the reactor pressure is reduced to 0.2 Torr in the above embodiment, it is impossible to selectively etch SiO.sub.2 from Si even with a partial pressure ratio [H.sub.2 O]/[SF.sub.6] exceeding 1.

DEPR:

Although the above embodiment produces SO.sub.3 by a reaction of active species generated by electric discharge in a mixture of SF.sub.6 and H.sub.2 O gases, it is possible to use a rare SO.sub.3 gas or oxidize a sulfur gas. Instead of SF.sub.6, other gases such as F.sub.2, C.sub.x F.sub.y, C.sub.x F.sub.y H.sub.z, NF.sub.3, BF.sub.3, PF.sub.x, SF.sub.x Cl.sub.y and SF.sub.x O.sub.y may be used, and instead of H.sub.2 O, a mixture of H.sub.2 and O.sub.2 gases may be used. In addition, gases containing elements H, O, F and S may be employed and reacted to form a condensed layer of HF and H.sub.2 SO.sub.4 on the surface of a sample to etch an oxide film of the sample.

DEPR:

In the above embodiment, HF is dissolved in H.sub.2 SO.sub.4. It is possible to dissolve HF in a liquid of inorganic compounds such as H.sub.2 O, H.sub.-2 SO.sub.3, HNO.sub.3, HNO.sub.2 H.sub.2 CO.sub.3, H.sub.3 PO.sub.4, H.sub.3 BO.sub.3, H.sub.3 AsO.sub.4, NCH, CH.sub.3 CN, H.sub.2 S and POCl.sub.3 or of organic compounds such as CH.sub.3 OH,

C.sub.2 H.sub.5 OH, C.sub.3 H.sub.8 and (C.sub.2 H.sub.5).sub.2 O to be formed on the surface of a sample. These liquids are formed by activating and reacting gases containing all of component elements.

DEPR:

Instead of dissolving HF in other liquids, HF may be combined with gases such as BF.sub.3, PF.sub.5 and SO.sub.3 to form liquids such as HBF.sub.4, HPF.sub.6 and HSO.sub.3 F on the surface of a sample to etch an oxide film of the sample.

DEPR:

In the above embodiment, a mixture of SF.sub.5 and H.sub.2 O gases is discharged. Instead, the electric discharge may be carried out within only one of the gases. Thereafter, the gases are reacted in a reactor. Gases may be activated not only by the electric discharge but also by optical radiation, heating and a reaction with charged particles and neutral active species. If a gas that spontaneously dissociates to produce active species containing halogen elements is used, an activation of the gas is not necessarily needed. For example, a combination of XeF.sub.2, SO.sub.3 and H.sub.2 O gases demonstrates a similar reaction as that of the above embodiment only by mixing the gases, in etching SiO.sub.2.

CLPR:

3. The method as claimed in claim 2, wherein said liquid is produced by dissolving said reactive gas in one of H.sub.2 O, H.sub.2 SO.sub.3, HNO.sub.3, HNO.sub.2 H.sub.2 CO.sub.3, H.sub.3 PO.sub.4, H.sub.3 BO.sub.3, H.sub.3 A.sub.s O.sub.4, HCN, CH.sub.3 CN, H.sub.2 S, POCl.sub.3, CH.sub.3 OH, C.sub.2 H.sub.5 OH, C.sub.3 H.sub.8 and (CH.sub.2 H.sub.5).sub.2 O.

CCXR:

134/1

CCXR:

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Document Number 1

Entry 1 of 27

File: USPT

Dec 16, 1997

US-PAT-NO: 5698070

DOCUMENT-IDENTIFIER: US 5698070 A

TITLE: Method of etching film formed on semiconductor wafer

DATE-ISSUED: December 16, 1997

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirano; Yoshihisa	Tokyo	N/A	N/A	JPX
Tahara; Yoshifumi	Tokyo	N/A	N/A	JPX
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Horioka; Keiji	Tokyo	N/A	N/A	JPX

US-CL-CURRENT: 1/1; 156/345

ABSTRACT:

A method of etching oxide film on a semiconductor wafer comprising pushing the wafer against the top of lower electrode while facing it to an upper electrode, decompressing to exhaust a chamber, forming electric field between the wafer and the upper electrode under decompressed state and generating the gas plasma of process gas while supplying the process gas to an oxide-film-formed surface of the wafer through the upper electrode, introducing auxiliary gas to the peripheral portion of the wafer when the gas plasma of process gas is acting on the wafer, and controlling the etching reaction of the gas plasma relative to the peripheral portion of the wafer by auxiliary gas.

47 Claims, 19 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 17

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Document Number 1

Entry 1 of 1

File: USPT

Jun 9, 1998

DOCUMENT-IDENTIFIER: US 5763016 A

TITLE: Method of forming patterns in organic coatings films and layers

ABPL:

Water-free, gaseous sulfur trioxide is used as an agent to form patterns in organic coatings, films, and layers, including photoresists, by etching areas exposed to the agent through an overlying mask or by developing a latent image of the desired pattern using the agent as a dry-developer.

BSPR:

U.S. Pat. No. 5,037,506, issued Aug. 6, 1991, to S. Gupta et al and entitled "Method of Stripping Layers of Organic Materials", discloses and claims the use of gaseous sulfur trioxide to remove various organic coatings, polymerized photoresist, and especially implant and deep-UV hardened resist layers, during the manufacture of semiconductor or ceramic devices. While the method disclosed or claimed in this patent is useful, there are further needs for selectively removing parts of such coatings, so as to create a predetermined pattern in the remaining organic coating.

BSPR:

In accordance with the invention, a reactive agent comprising sulfur trioxide and, optionally, other process gases is used to differentially oxidize, sulfonate, or otherwise react to cause selected parts of a masked image of a pattern, or a latent image of a pattern, contained in all types of organic coatings, films, and layers, including photosensitive and non-photosensitive organic materials, polymerized photoresists, paints, resins, multilayer organic polymers, certain organo-metallic complexes, positive optical photoresist, negative optical photoresist, electron-beam photoresists, X-ray photoresists, and ion-beam photoresists to be substantially completely removable by subsequent chemical or physical treatment.

BSPR:

In the case that a latent image of the desired pattern is reproduced in the coating, it is reproduced by projecting an image of the pattern on the coating with either (1) property-modifying, electromagnetic radiation including infrared, ultraviolet, and/or high-energy wavelengths as provided by E-beam or X-ray exposure, or (2) a property-modifying ion-beam. Alternatively, the latent image of the desired pattern may be reproduced in the coating through a conformal organic or inorganic mask of the desired pattern which is first reproduced on the surface of the coating by means of evaporation, sputtering, use of a multi-level resist process, plasma etching, or other masking method. The latent image of the desired pattern is then prepared in the coating by exposing the coating to a property-modifying precursor treatment, such as exposure to a gas such as water vapor, thus allowing water to be absorbed into the exposed region of the organic film, thereby increasing the water content of that region of the organic film and changing its reaction rate characteristics with sulfur trioxide gas.

BSPR:

The coated substrate, containing either the latent image of a desired pattern in the coating, or a conformal masking pattern on the surface of the coating, is exposed to the sulfur trioxide and other process gases which differentially react with the exposed organic coating, thus causing the desired portion of the organic coating to be substantially removable by subsequent chemical or physical treatment. The reactive power of the process gases may be usefully modified (1) by reducing the concentration of the appropriate agent at an appropriate time in the process, (2) through the addition of various gases at an appropriate time in the process, (3) through the addition of heat to the process at an appropriate time in the process, or (4) through the use of an end-point detector to selectively stop the reaction as required.

BSPR:

Differential reaction of the organic coating with the process gases may thus be controlled by (1) changing the reaction rate properties of the different parts of the latent image in the coating, film or layer; (2) protecting selected parts of the coating from development by means of a conformal mask on the surface of the coating; and by (3) changing the reactive power of the process gases which may include sulfur trioxide gas.

BSPR:

After initial flushing with inert gases, substrates containing either latent images in the coating, or masked patterns on the surface of the coating, are exposed to regulated quantities of gaseous sulfur trioxide and other process gases. These gases are dispensed into chambers, or a series of closed chambers with good vacuum integrity, which contain the substrates. Additional chemical and physical treatment may be required prior to, during, and/or subsequent to exposure to these process gases for the purpose of improving the effectiveness of the method. Liquid or solid sulfur trioxide, whether in alpha, beta, or gamma form, or a mixture thereof, may be stored and used as the source of vapor. Sulfur trioxide is an extremely strong oxidizing and sulfonating chemical, and is very effective as an agent in removing a variety of organic materials. Being in a gas phase, it achieves a more thorough contact with the surfaces of submicrometer grooves and crevices than is possible by liquid development solutions. Being in a gas phase, it is also more quickly introduced and removed from the reaction interface when desired; under the correct conditions of this invention, it is less subject to depletion at the reaction interface; it is less likely to introduce contaminants than liquid phase developers; and it is more easily maintained in a homogeneous state during the development process.

DEPR:

The basic concept behind this invention is that a novel chemical agent, under the correct processing conditions and comprising essentially of sulfur trioxide, is used in gaseous form to dry-etch a masked pattern, or to dry-develop a latent image, that may be contained in all types of organic coatings, films, and layers, including photosensitive and non-photosensitive organic materials, polymerized photoresists, paints, resins, multilayer organic polymers, certain organo-metallic complexes, positive optical photoresist, negative optical photoresist, electron-beam photoresists, X-ray photoresists, and ion-beam photoresists. An example of such a latent image in a non-photosensitive coating, film or layer would include material where a latent image is defined by its chemical composition or water content, possibly created by exposure to reactive gases or water vapor through a conformal mask or multi-level resist process, thus modifying the physical properties of the film, and its differential sensitivity to reaction with the process gases, in the exposed areas. A conventional method, included here as an example, for creating such a latent image in a photosensitive coating, film or layer would include a coating where the latent image is defined by its molecular weight and thus by its physical properties, including its reaction characteristics with the process gases, in the exposed areas. The method is thus controlled by changing the reaction characteristics of different areas of the pattern or latent image when

exposed to the sulfur trioxide process gases, and/or by changing the reactive power of the process gases, including sulfur trioxide, during the development reaction.

DEPR:

The gaseous form of sulfur trioxide, coupled with its reactive power under certain conditions, is an agent which provides for differential reaction with, and removal of, a variety of properly treated organic coatings, films and layers from submicrometer grooves and crevices which may be inaccessible to liquids. Being in the gaseous phase, it does not suffer from surface tension and capillary-action problems which limit the action of liquid developers by preventing contact with the walls of submicrometer grooves and crevices. Also being in the gaseous phase, it suffers less from depletion and reaction-product build-up problems at the chemical interface which may limit the action of liquid developers. For these reasons, such a method may make possible the development of features in the organic coating, film or layer with (1) smaller dimensions, such as size and aspect-ratio; (2) improved feature uniformity; and (3) fewer areas of undeveloped residues.

DEPR:

In the method of the invention, sulfur trioxide, which may be in alpha form, beta form, gamma form or a mixture thereof, is stored and used as the primary oxidizing, sulfonating, and otherwise reactive agent. Gamma-sulfur trioxide, with a melting point of 16.80.degree. C., is the preferred form for sulfur trioxide to be used in the invention, and is the form in which SO.sub.3 exists when it is maintained in absolutely pure and anhydrous condition. In general, stabilized gamma-sulfur trioxide is used, where addition of a small quantity of inhibitor (stabilizer) prevents formation of the high melting-point beta (32.5.degree. C.) and alpha (62.3.degree. C.) forms. Gamma-sulfur trioxide is commercially available with such inhibitors. The stabilized sulfur trioxide can readily be remelted, if it is allowed to solidify. Both stabilized and unstabilized sulfur trioxide may be used in the method of this invention. Water-free, gaseous sulfur trioxide is employed in the selective removal of the organic films, coatings and layers. It is an important requirement of this method to minimize the water content of the sulfur trioxide gas at the correct time in the method and to control the water content during the practice of the method.

DEPR:

The dry-etch and dry-develop method of the invention is advantageously employed in both batch (multiple substrates) and single-substrate operation modes. In either case, regulated quantities of gaseous sulfur trioxide are dispensed, continuously, or at appropriate intervals, into closed, vacuum-sealed chamber(s), which are required primarily to minimize and control the moisture level. Moisture level may also be minimized and controlled by maintaining the walls of the chamber(s) at elevated temperatures. The flow rate and pressure of the sulfur trioxide gas and other process gases, and the time of exposure needed for the method will depend on the size of the chamber and the number of substrates, and their sizes, to be subjected to the method at one time. In some cases, it may be necessary to stop the development or etching reaction before the reactants are exhausted. In such cases, an end-point detector may be employed to determine when to stop the reaction. In the method of this invention, the reaction rate may be decreased or halted at the desired moment by, for example, (1) introducing additional, non-reactive gases to the chamber, such as nitrogen or argon, thus diluting the sulfur trioxide so as to decrease the reactive power of the gases in the chamber; or (2) reducing the temperature of the reaction interface by reducing the temperature of the substrate; or (3) by removing the substrate from the processing chamber; or (4) by removing the reactive process gases from the process chamber. The reaction rate may be increased at the desired moment by, for example, (1) introducing additional process gases to the chamber, such as anhydrous sulfur trioxide, so as to increase the reactive power of the gases in the chamber; or (2) increasing the temperature of the reaction interface by heating the substrate.

DEPR:

After introduction of the substrate containing the masked pattern or the latent image into the process chamber, the chamber is purged, one or several times, with dry, inert gas, such as nitrogen or one of the commonly used inert gases. The chamber is then evacuated to a suitable vacuum, such as on the order of about 10^{-3} Torr. Water-free, gaseous sulfur trioxide is then introduced into the chamber as a reactive agent for differentially oxidizing, sulfonating or otherwise reacting with the different areas on the organic coating, film or layer as defined by the masked pattern or the latent image. The directional flow of the process gases through the processing mechanism is controlled by means of the physical design of the process chamber in order to improve the effectiveness of the method. Depending on the specific nature of the coating, other chemically reactive process gases may be dispensed in a similar fashion, either prior to the introduction of the sulfur trioxide gas, simultaneously with the sulfur trioxide gas, or subsequent to the introduction of the sulfur trioxide gas, for the purpose of improving the effectiveness of the method. The substrates introduced to the process chamber require specific physical treatment (for example, dry heating, exposure to high-energy electromagnetic radiation, rinsing in de-ionized water) either before, during or after exposure to the process gases for the purpose of improving the effectiveness of the method.

DEPR:

While the total time of exposure of the coated substrate to the gaseous sulfur trioxide and other process gases varies depending on several factors, the typical time of exposure is less than five minutes. These factors include (1) the reaction rate properties of the different areas in the masked pattern or in the latent image, (2) the thickness of the organic coating, film or layer, (3) the number of substrates in the process chamber, (4) the size of each substrate, (5) the reaction power of the process gases including sulfur trioxide (which is controllable over time), as well as (6) other processing conditions.

DEPR:

The substrate may be maintained at room temperature during exposure to the gaseous sulfur trioxide process gases or heated to an elevated temperature. If heated, the temperature is not a limitation of the method. Temperature of the substrate and the processing environment is controlled, and may be limited, in order to improve the effectiveness of the method. Typically, the temperature range is between room temperature and 400.degree. C.

DEPR:

Following differential reaction of the masked pattern on or the latent image contained in the organic coating, film or layer by exposure to the process gases, which may include gaseous sulfur trioxide, the substrate may be further treated with chemical and physical processes to remove any development reaction products. For example, the substrate may be rinsed in deionized water, treated with a high-frequency sound, both ultrasonic and megasonic, cleaning processes, sprayed with solvents such as the lower alkanols (1 to 5 carbon atoms), dipping in isopropyl alcohol, acetone, and mixtures thereof.

DEPR:

Without subscribing to a particular theory and independent of the details of the sulfur trioxide reactions, the underlying principle of operation of the invention is the differential sensitivity of all organic coatings, films and layers to this reaction, or reactions, at different rates based upon different physical properties between different areas in the masked pattern or in the latent image, and upon controllable changes to the reactive power of the sulfur trioxide process gases over time. The method of the invention can be carried out whether sulfur trioxide is used in the form of pure or stabilized gas, or vaporized from a pure or stabilized liquid sulfur trioxide. The method of the invention equally applies when the reactivity of the sulfur trioxide vapor is obtained from a mixture of chemical substances,